



Corrosion of pure magnesium and AZ31 magnesium alloy in choline chloride : ethylene glycol deep eutectic solvent

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Ionic Liquids (IL)

Ionic liquids are salts with melting point of 100°C and below.
Consist solely of cations and anions, with no solvent molecules.

PROPERTIES

- High conductivity,
- Extremely low vapour pressures,
- Low viscosity,
- High temperature stability,
- Low toxicity,
- Non flammability,
- Wide electrochemical window,
- Liquid in a broad range of temperatures.

APPLICATIONS

- Electrodeposition of metals,
- Electrolytes for electrochemical capacitors, fuel cells, solar cells, Li ion batteries,...
- Fluids for thermal storage and exchange in solar power plants,
- Solvents and catalysts in organic and inorganic synthesis.

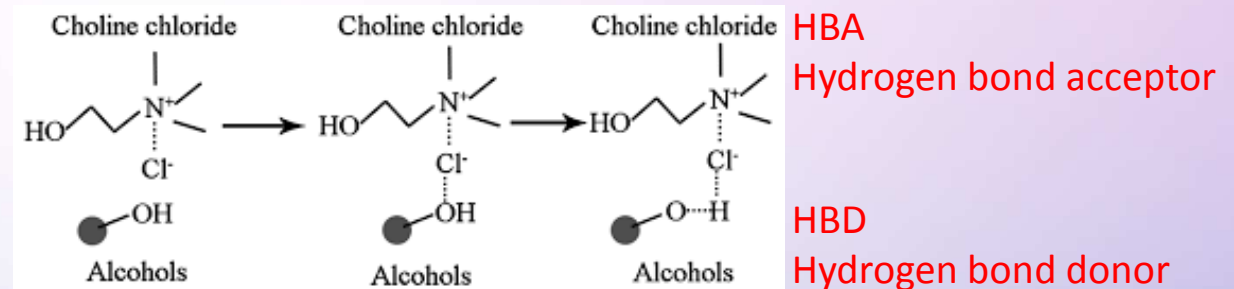
DEEP EUTECTIC SOLVENTS (DES)

- DES are eutectic mixtures which form homogeneous liquids through hydrogen bonding.

Tomé *et al.*, *Applied Materials Today* 10 (2018) 30–50

2.3. DES vs IL

IL first appeared at the beginning of the 20th century but their importance as convenient green alternatives to common organic solvents was only recognized much later [58–61]. Despite the early enthusiasm, testified by the boom in publications in the decade 2000–2010 [59,60,62], some of their initially assumed advantageous characteristics soon started to be questioned [60–62]. In this context, DES emerged as versatile substitutes for conventional IL, and were initially treated as a new generation of IL [4]. Although they have similar physicochemical properties to IL, DES differ from IL in three main aspects [4–7,9–14]. First, the potential for scale-up: IL are expensive, and some of them present high toxicity, as well as having poor biodegradability, biocompatibility and sustainability [60–62]. By contrast, DES have lower costs and a much-reduced environmental impact. Secondly, the preparation processes of IL and DES are quite different. While DES are synthesized by simply mixing the components, generating no waste and requiring no purification steps, the preparation of IL is far more difficult and expensive. Finally, IL are composed entirely of ions, that interact through ionic bonds; DES are the result of complexation between a HBA and a HBD whose interactions, as discussed above, involve mostly hydrogen bonds.



The main applications of DESs include:

- Energy storage,
- Electrodeposition,
- Electropolishing,
- Homogeneous catalysis,
- Analytical chemistry,
- Biocatalytic processes,
- CO₂ capture.

Corrosion in DES

Prog. Nat. Sci.: Mater. Int. 25 (2015) 595

Electrochem. Commun. 90 (2018) 101

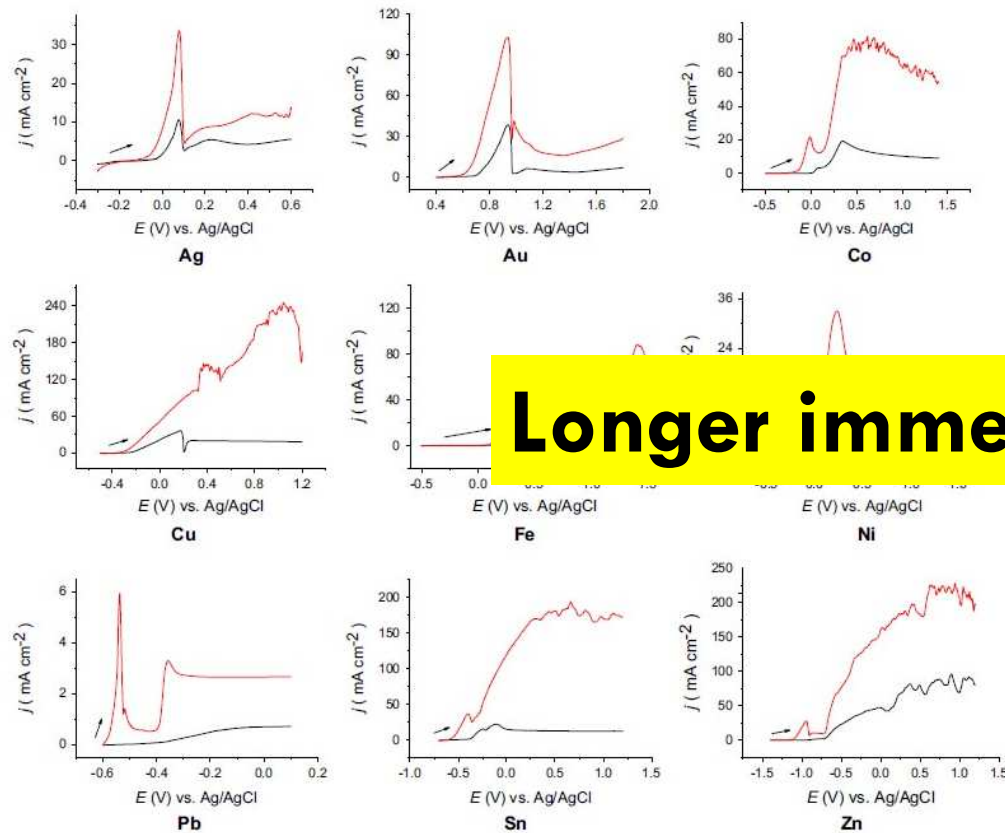
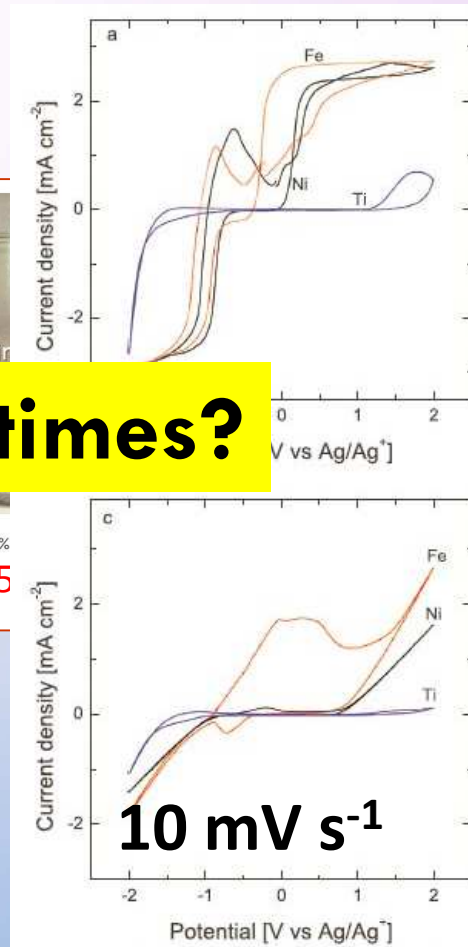


Fig. 1. LSVs of (from top left) Ag, Au, Co, Cu, Fe, Ni, Pb, Sn and Zn in Ethaline at 20 (black line) and 70 °C (red line). The sweep rate was 5 mV s⁻¹.

5 mV s⁻¹

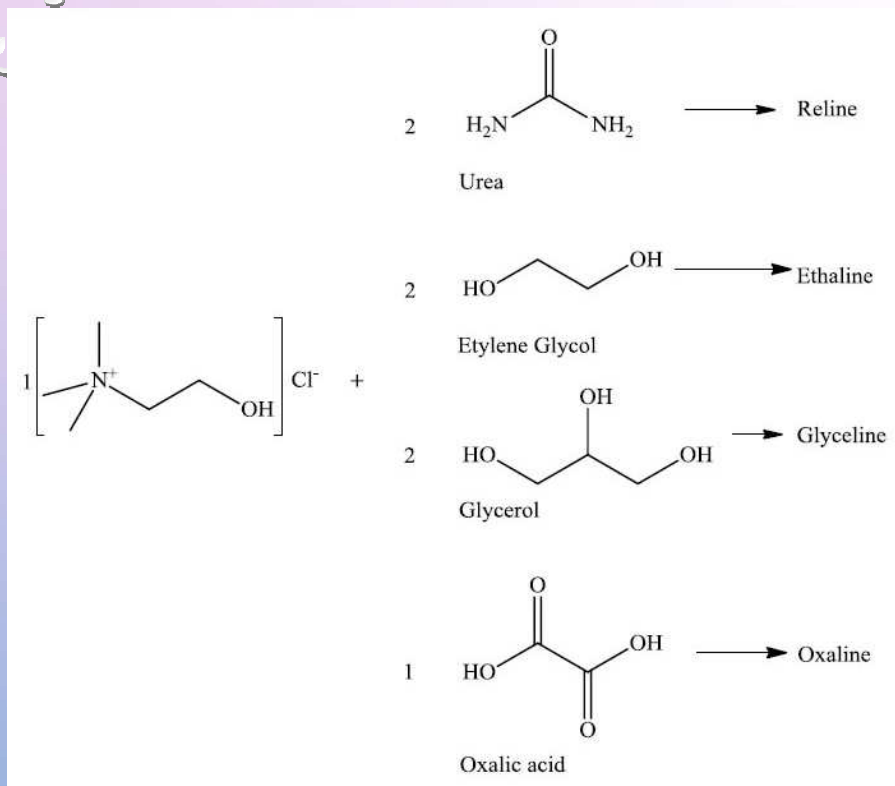


1 mineral base oil containing 1%
16 (2014) 415



10 mV s⁻¹

DEEP EUTECTIC SOLVENTS (DES)



Physical properties

	Viscosity (mm ² s ⁻¹)		d (25 °C) (g cm ⁻³)	T _f (°C)	Surface tension (mN m ⁻¹)
	40 °C	100 °C			
Reline	218	24	1.20	12	86.4
Ethaline	20	5	1.12	-61	49.2
Glyceline	118	23	1.19	-35	55.4
Oxaline	149	28	1.20	-18	75.3

Taken from Abbott et al., *Green Chem* 16 (2014) 4156.

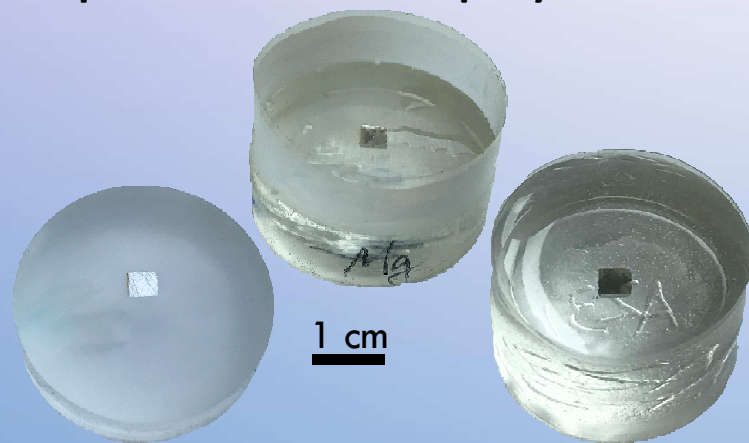
Corrosion of Mg and AZ31 in Ethaline (Some experimental details)

Ethaline

Prepared by mixing at 60 °C choline chloride and ethylene glycol at a molar ration of ChCl 1:2 EG.

Mg from Mateck (Germany)
AZ31 from Alubin (Israel)

Samples embedded in epoxy matrix



Methods and Techniques

Immersion and optical inspection

SVET

EIS

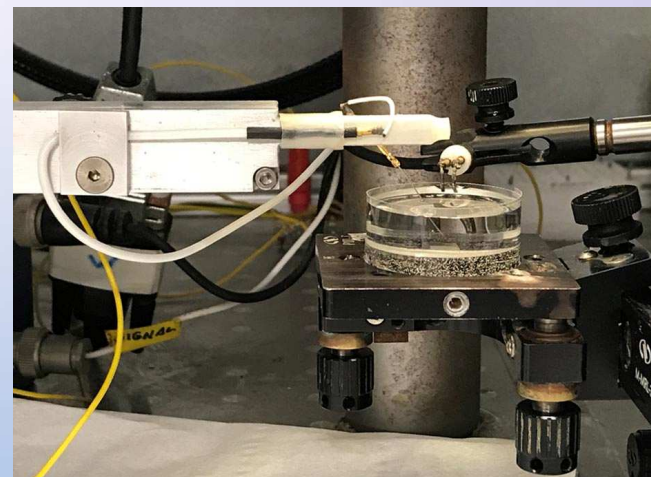
E-I curves

CV with 10 μ m Pt electrode close to surface

WE: $\sim 1\text{cm}^2$

RE: SCE, usually with salt bridge with ethaline

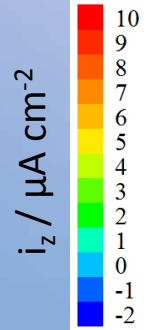
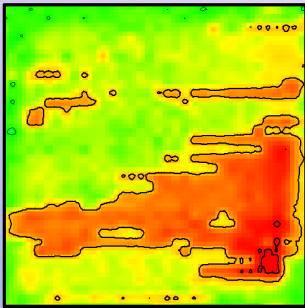
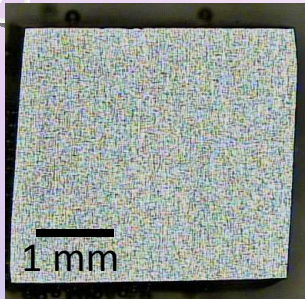
CE: Pt wire



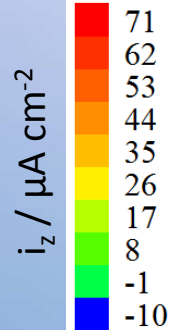
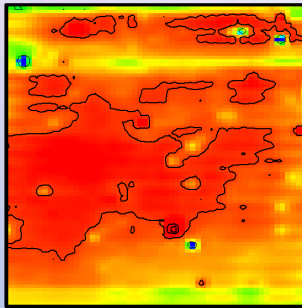
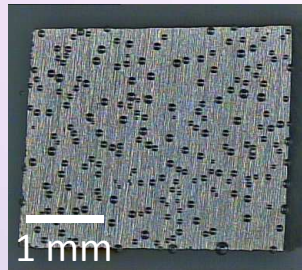
2-25 minutes of immersion

Magnesium

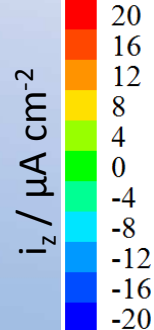
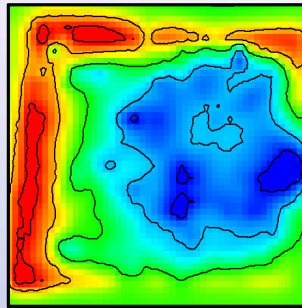
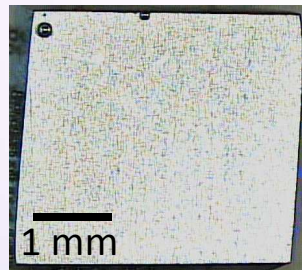
Ethaline



0.07M NaCl

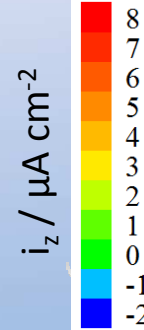
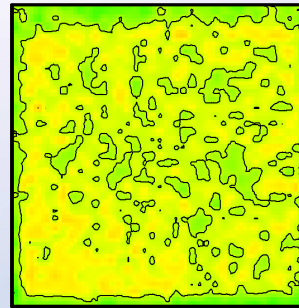
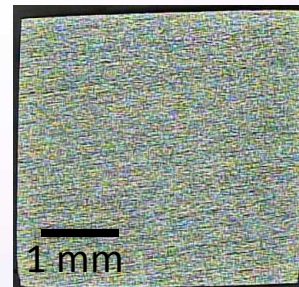


Deionised water

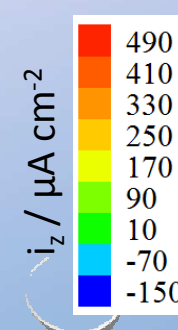
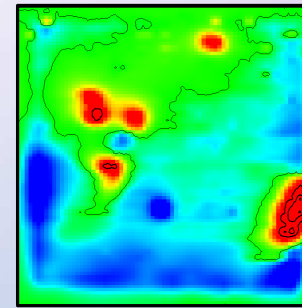
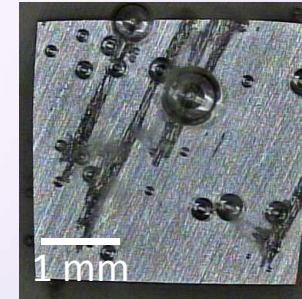


AZ31

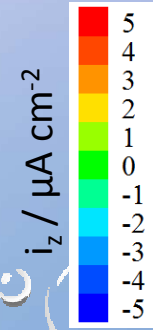
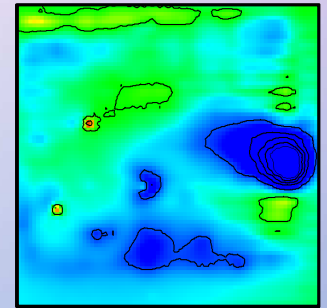
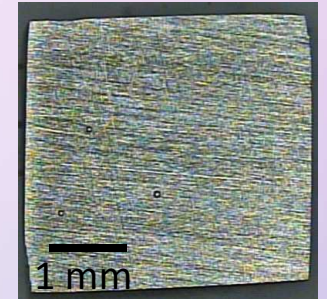
Ethaline



0.07M NaCl



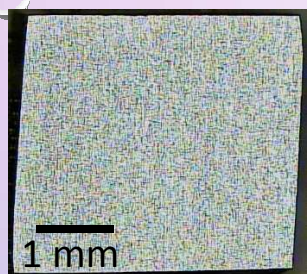
Deionised water



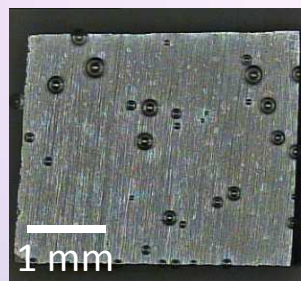
30-50 minutes of immersion

Magnesium

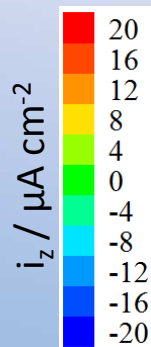
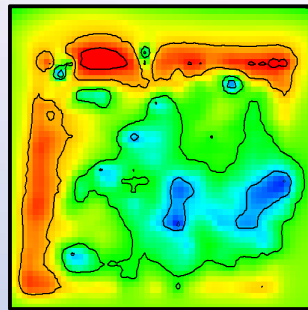
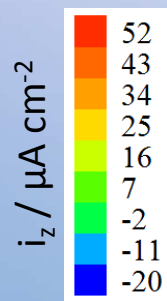
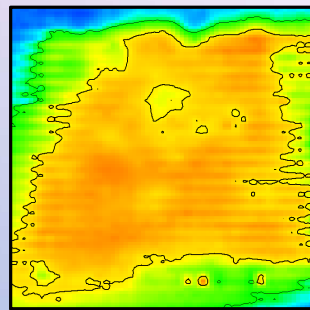
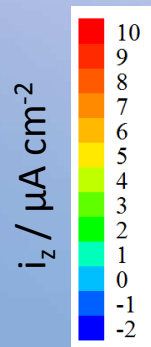
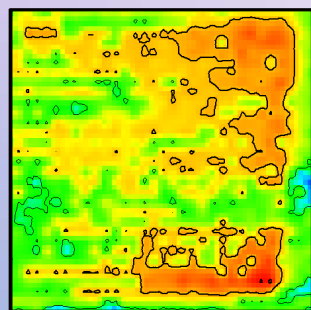
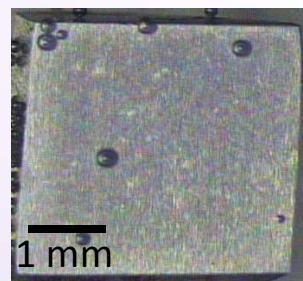
Ethaline



0.07M NaCl

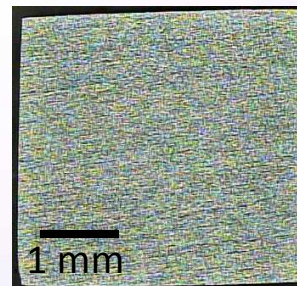


Deionised water

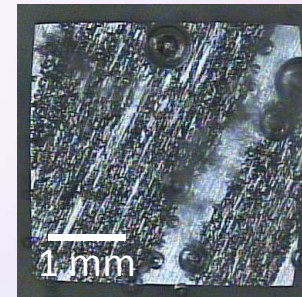


AZ31

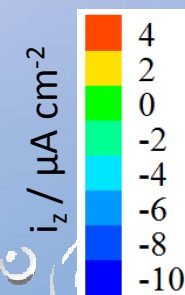
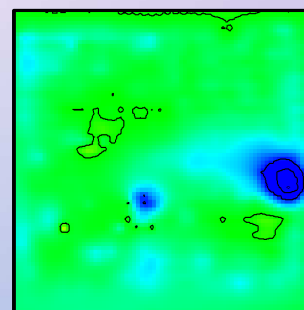
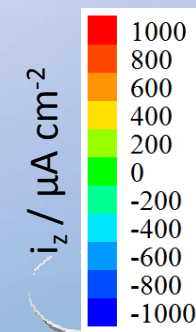
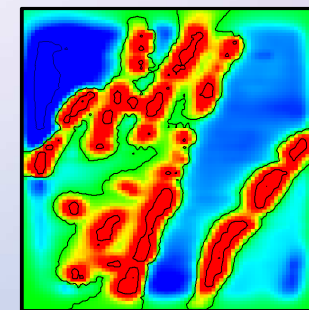
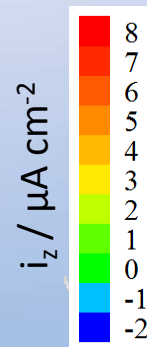
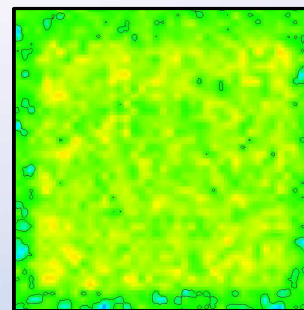
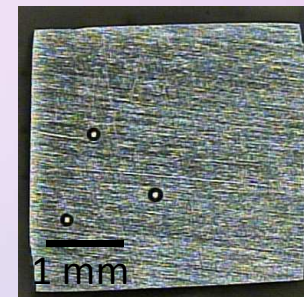
Ethaline



0.07M NaCl



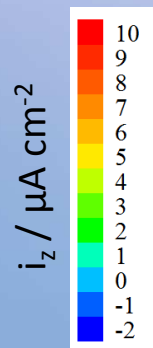
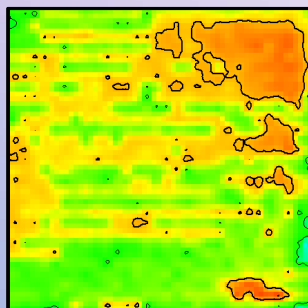
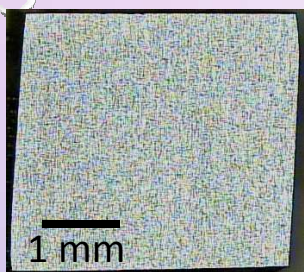
Deionised water



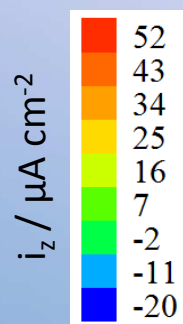
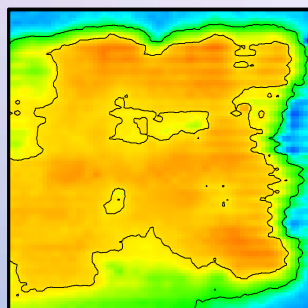
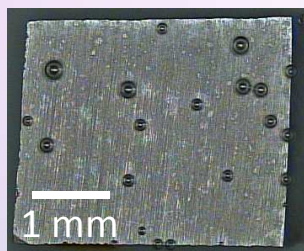
1 hour of immersion

Magnesium

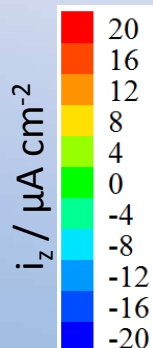
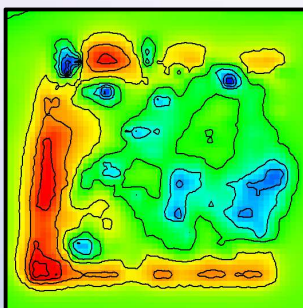
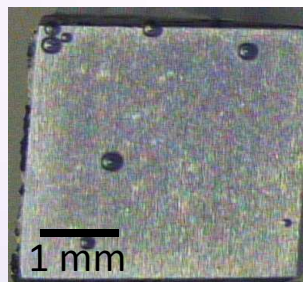
Ethaline



0.07M NaCl

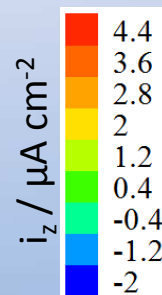
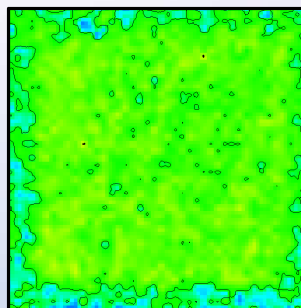
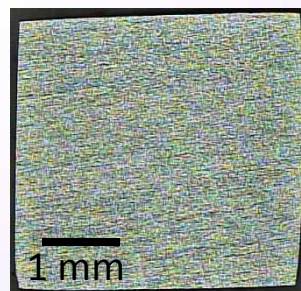


Deionised water

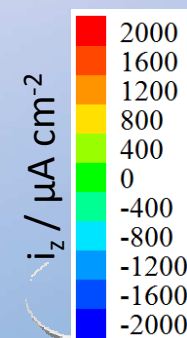
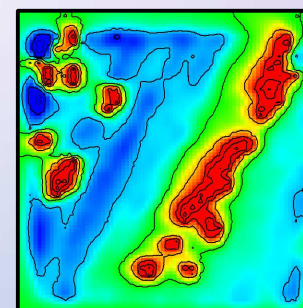
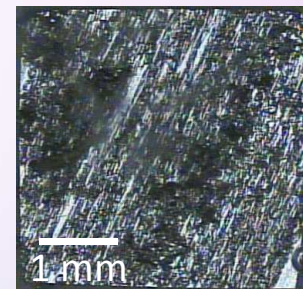


AZ31

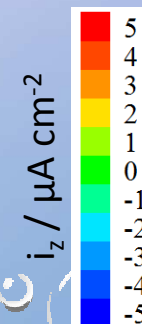
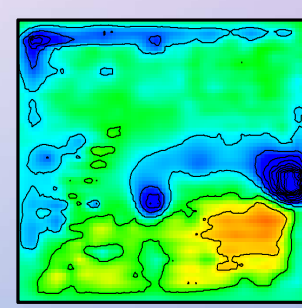
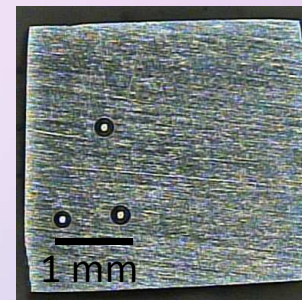
Ethaline



0.07M NaCl



Deionised water



1 day of immersion

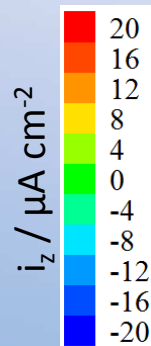
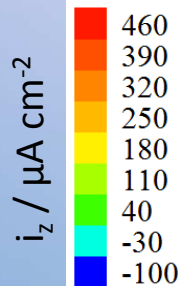
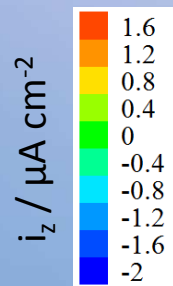
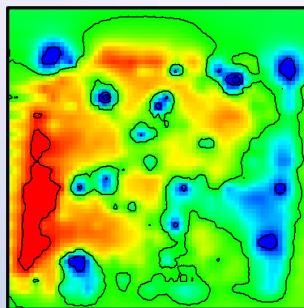
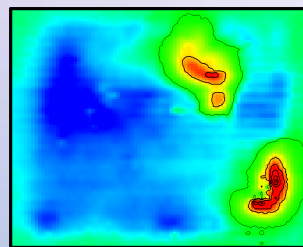
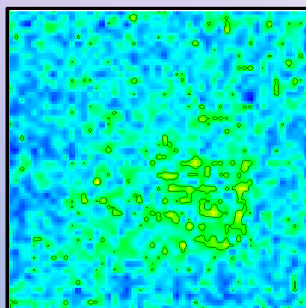
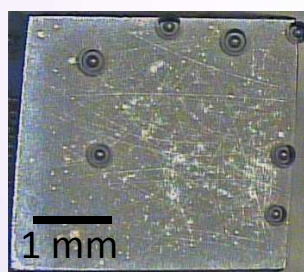
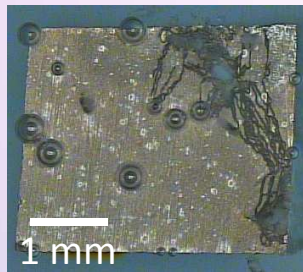
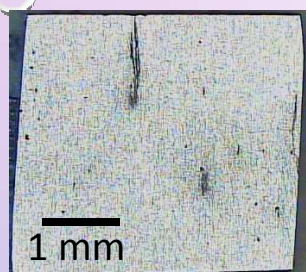
Magnesium

AZ31

Ethaline

0.07M NaCl

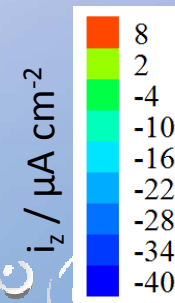
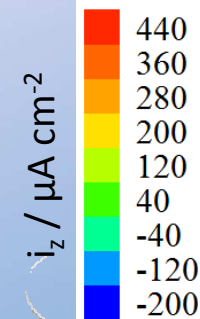
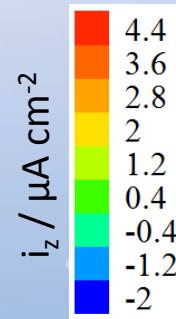
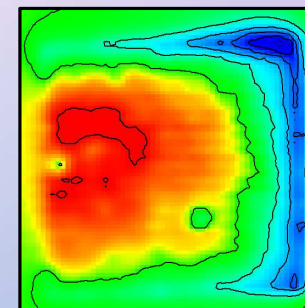
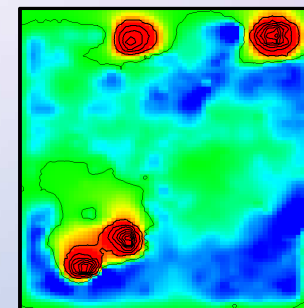
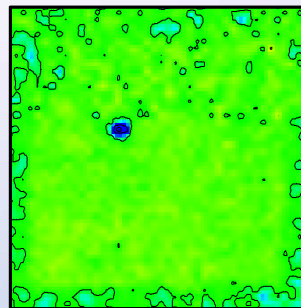
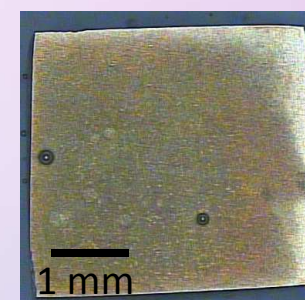
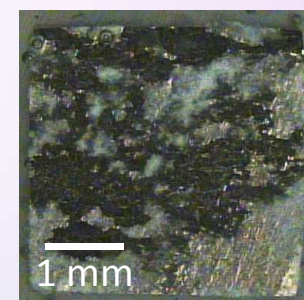
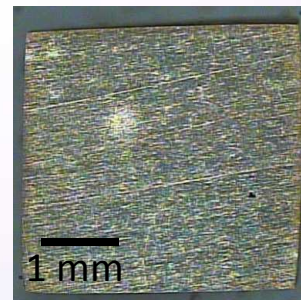
Deionised water



Ethaline

0.07M NaCl

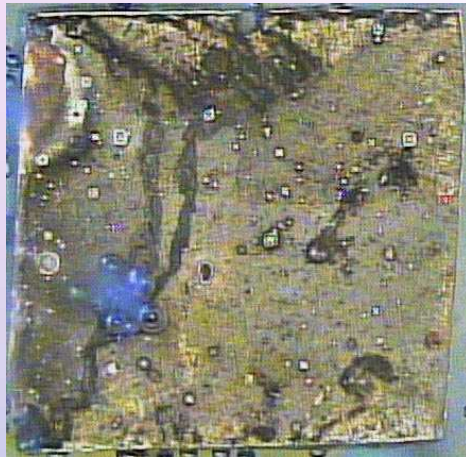
Deionised water



20 days of immersion

Magnesium

1 mm



Ethaline
open to air

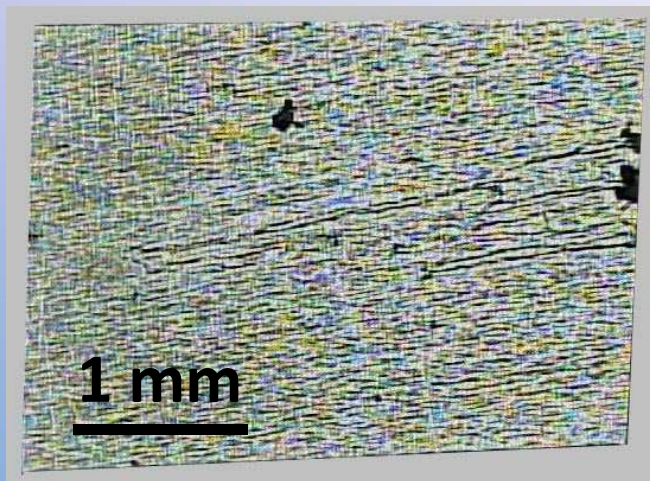
AZ31

1 mm

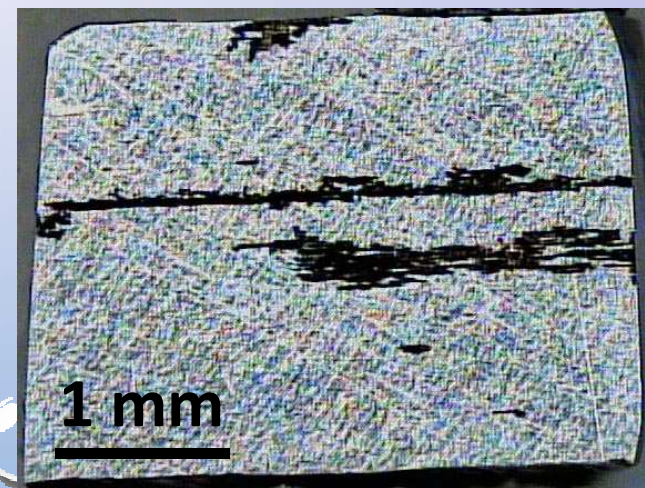


Ethaline
in closed
container

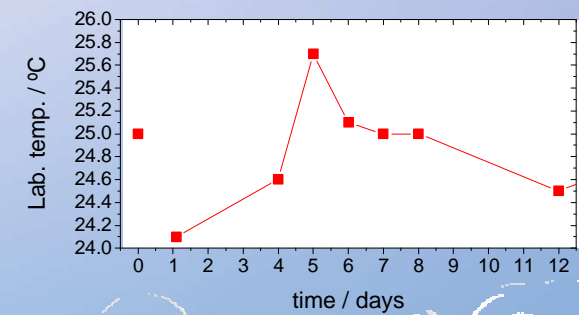
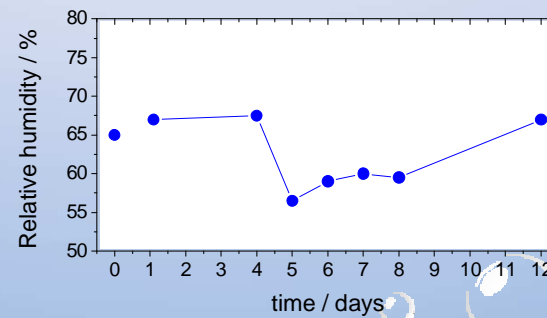
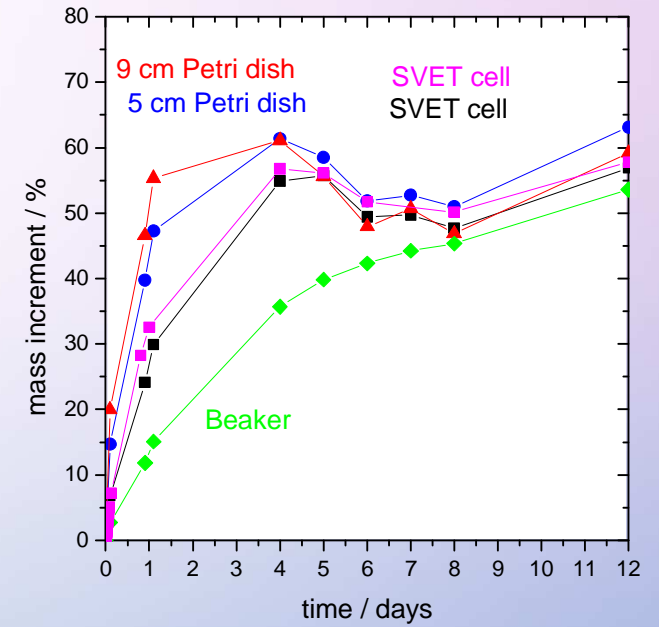
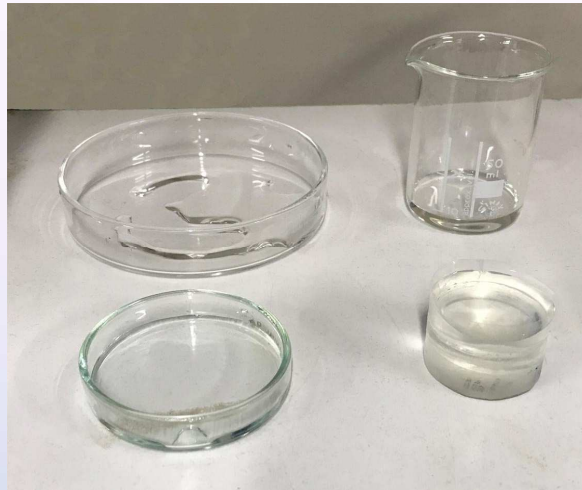
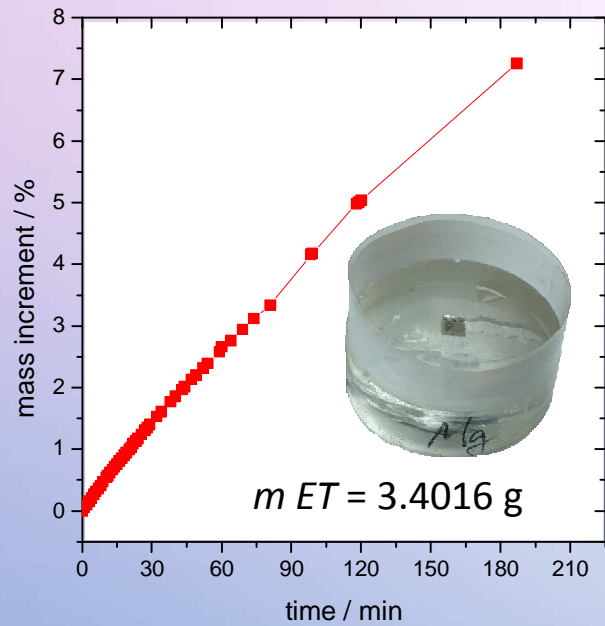
1 mm



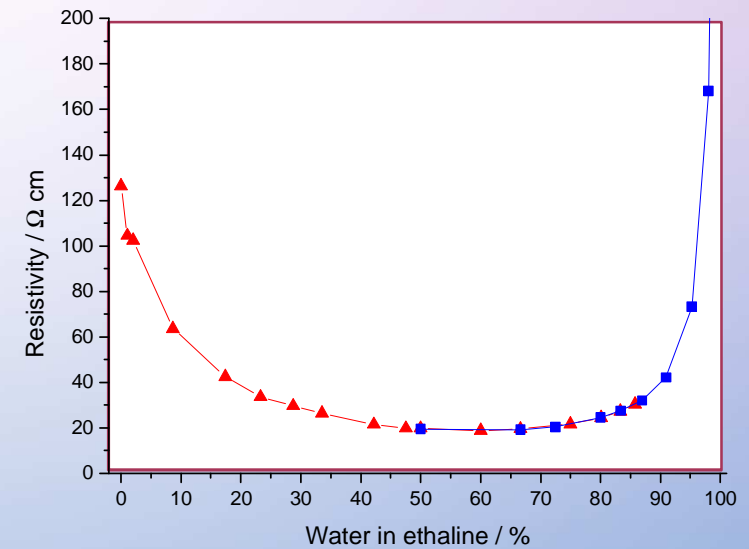
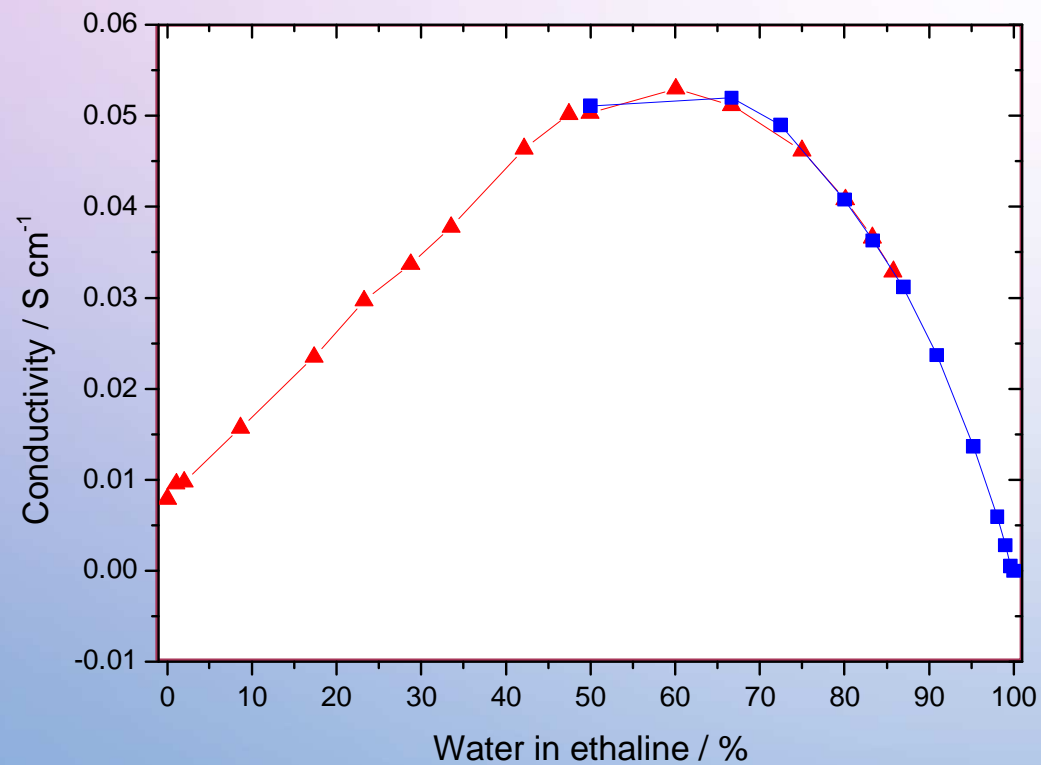
1 mm



Water pick-up



Conductivity of the mixture ethaline - water



2-25 minutes of immersion

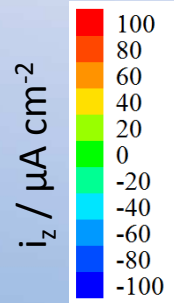
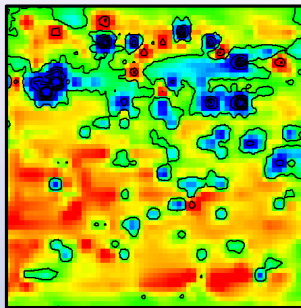
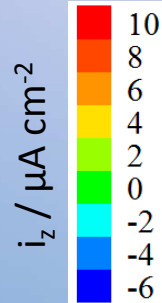
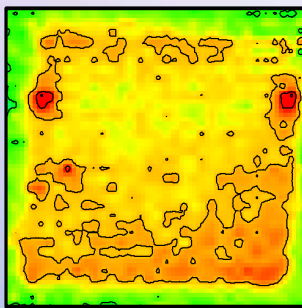
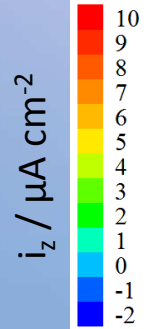
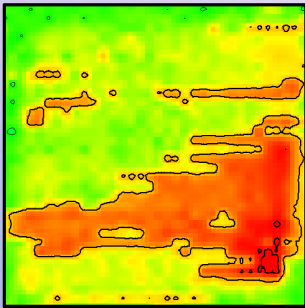
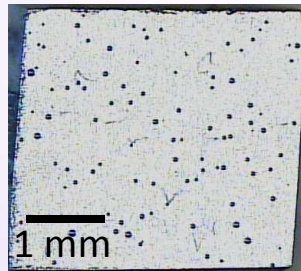
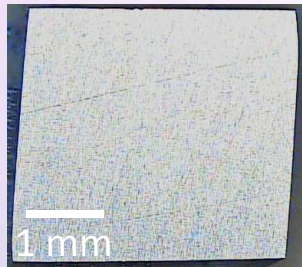
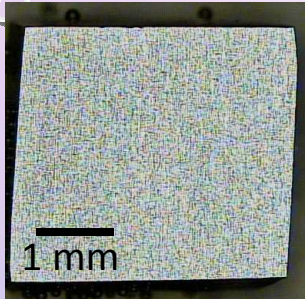
Magnesium

AZ31

Ethaline

5% water

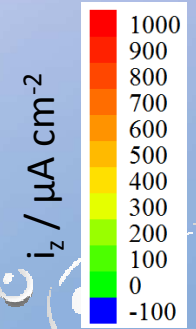
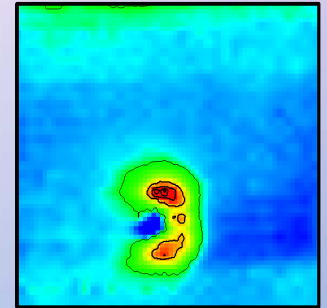
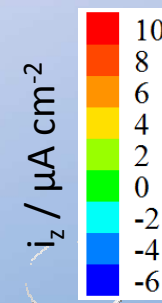
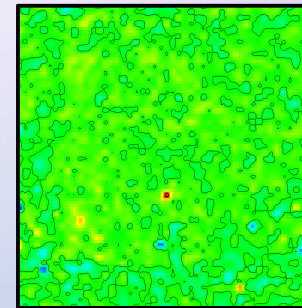
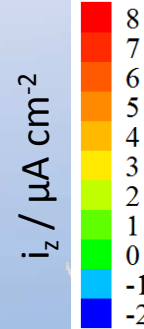
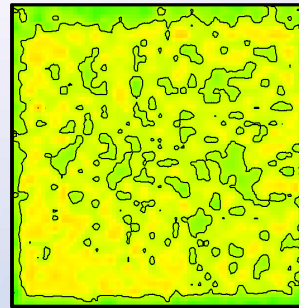
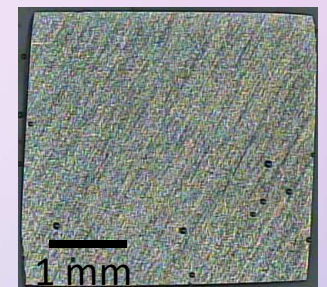
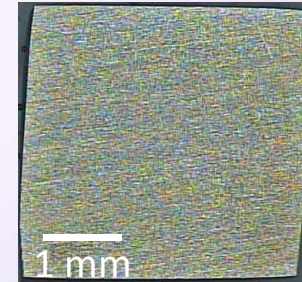
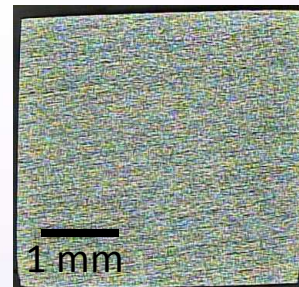
50% water



Ethaline

5% water

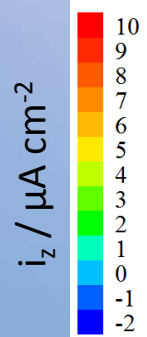
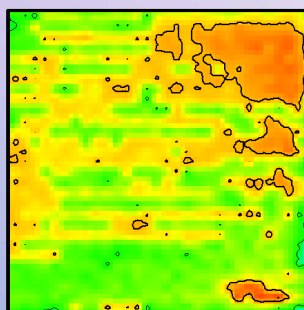
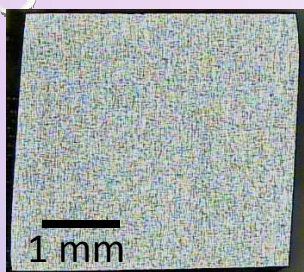
50% water



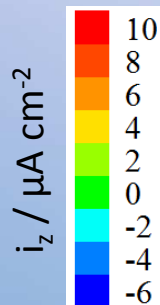
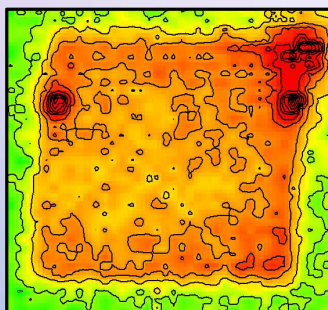
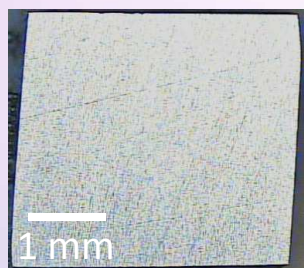
1 hour of immersion

Magnesium

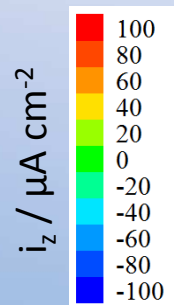
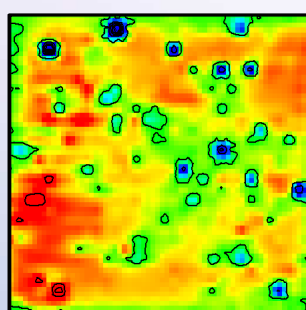
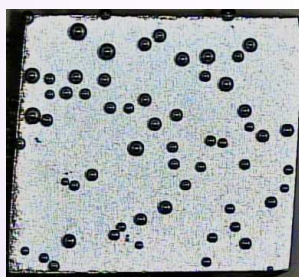
Ethaline



5% water

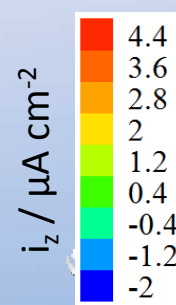
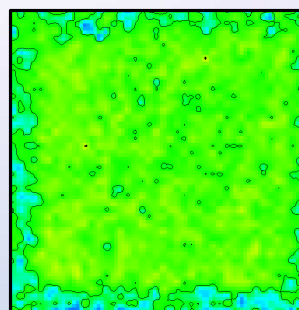
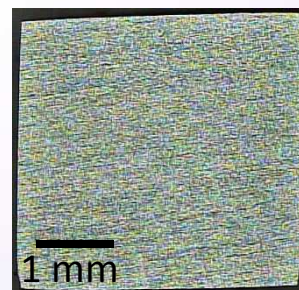


50% water

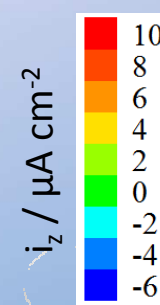
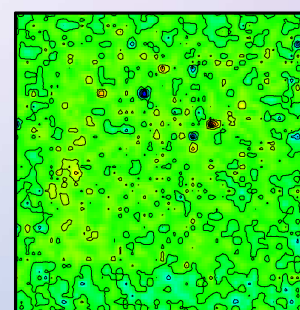
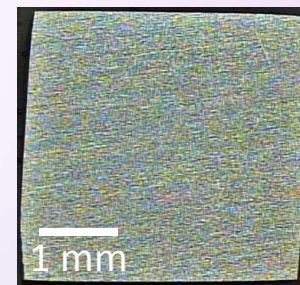


AZ31

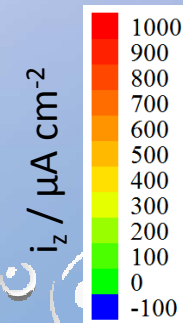
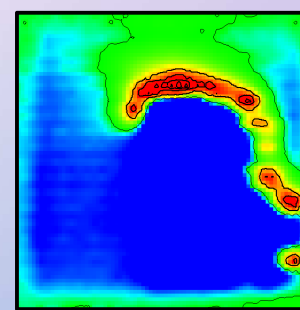
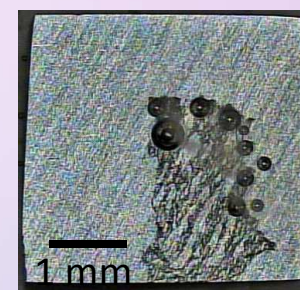
Ethaline



5% water



50% water



1 day of immersion

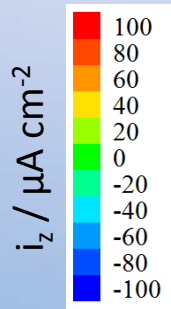
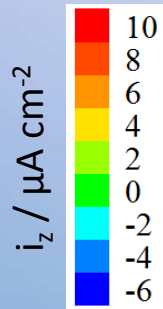
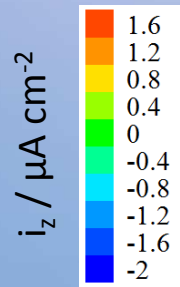
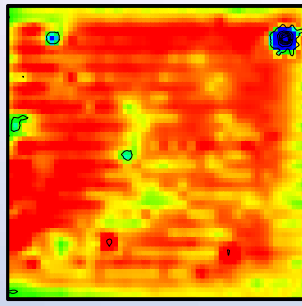
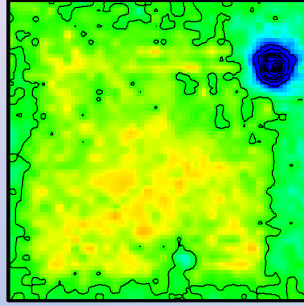
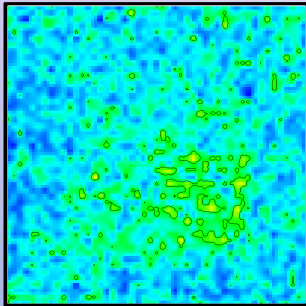
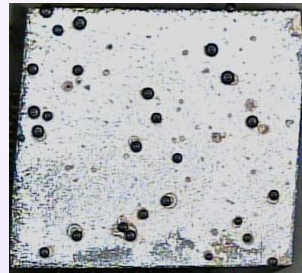
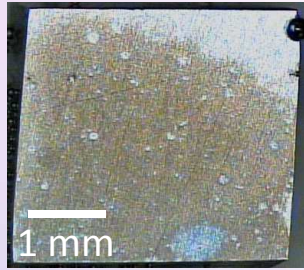
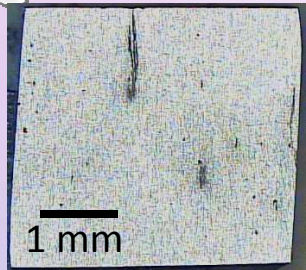
Magnesium

AZ31

Ethaline

5% water

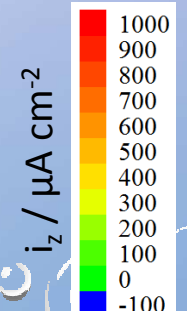
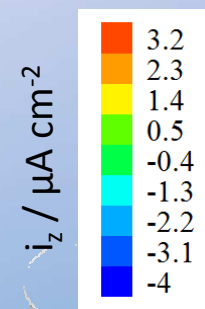
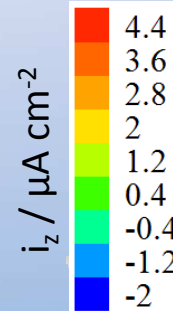
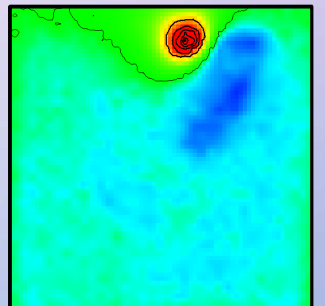
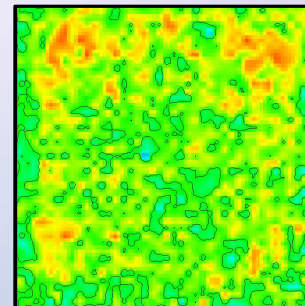
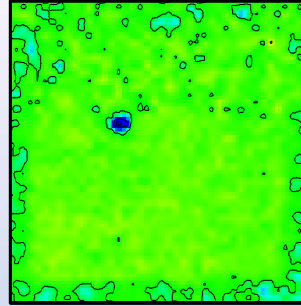
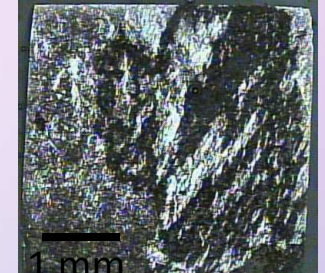
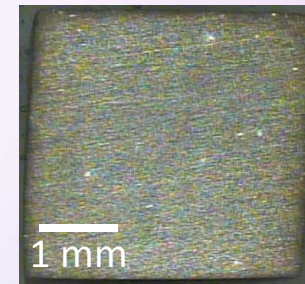
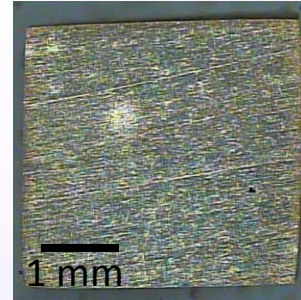
50% water



Ethaline

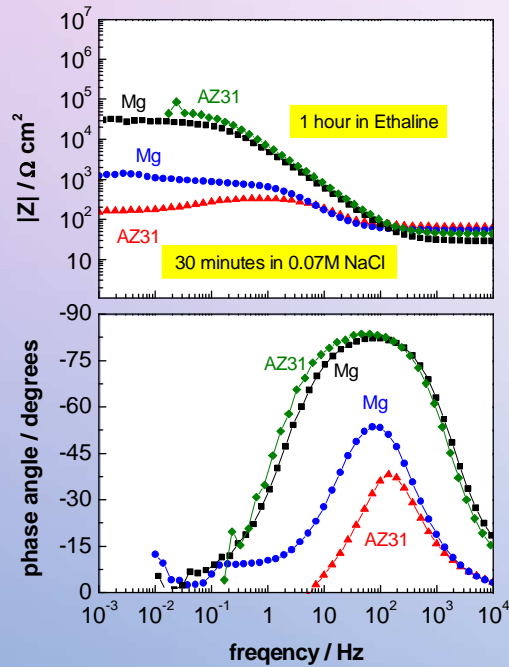
5% water

50% water

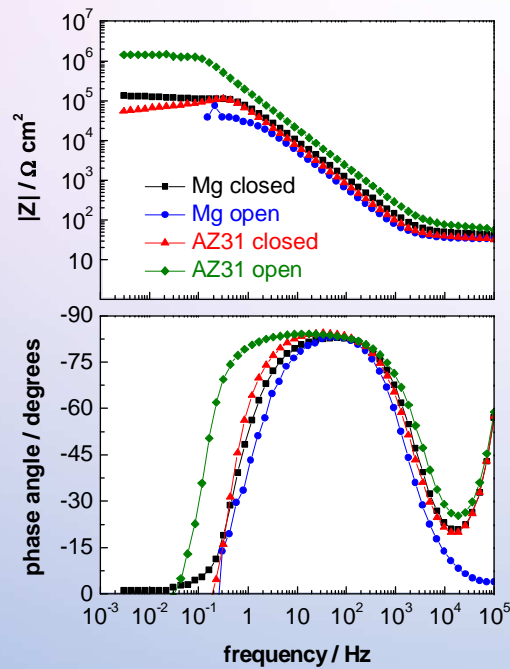


Electrochemical Impedance Spectroscopy

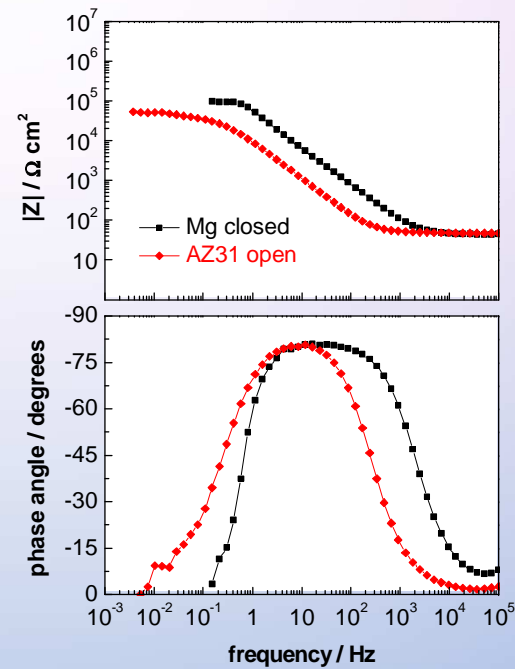
~1 hour in
0.07M NaCl and in ET



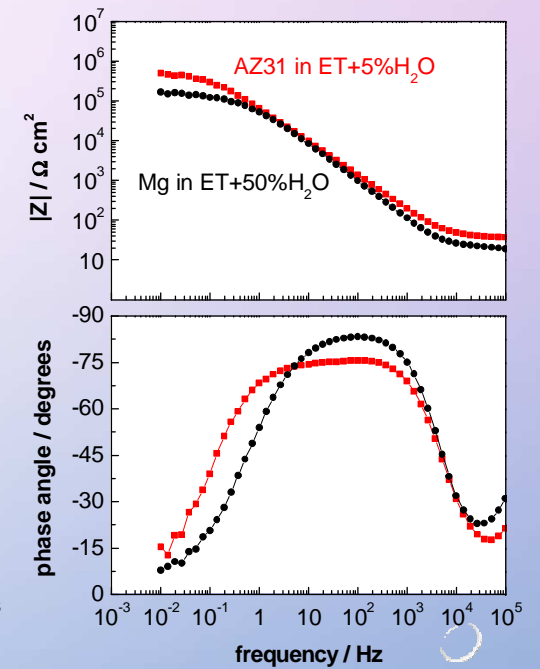
1 day in ET



18 days in ET

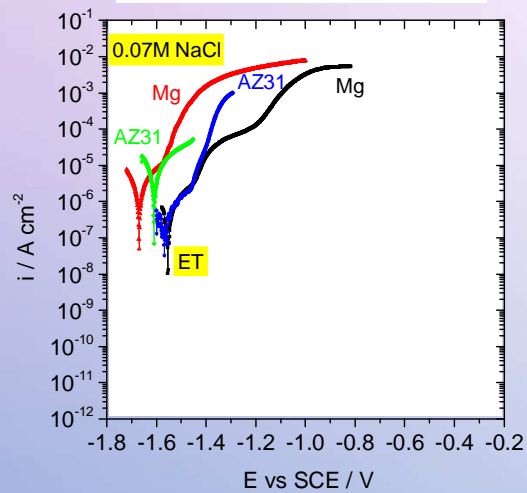


1 day in ET+H₂O

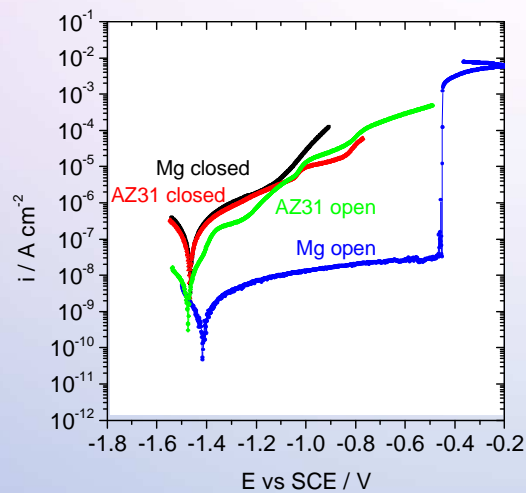


E - log i response

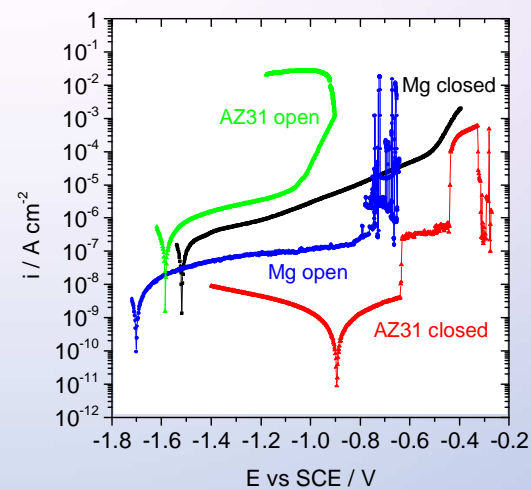
After 1 hour in
0.07M NaCl and ET



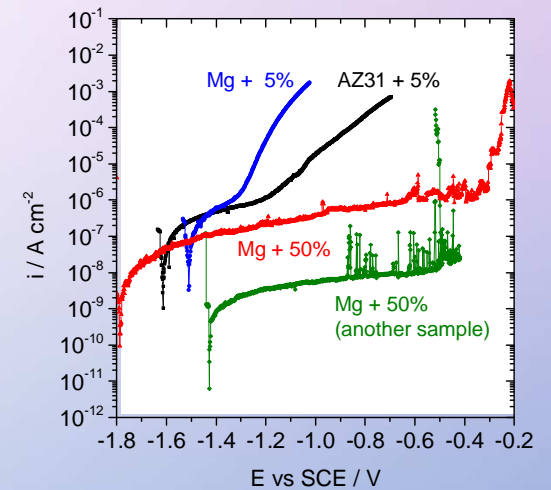
In ET after 24h



In ET after 18 days

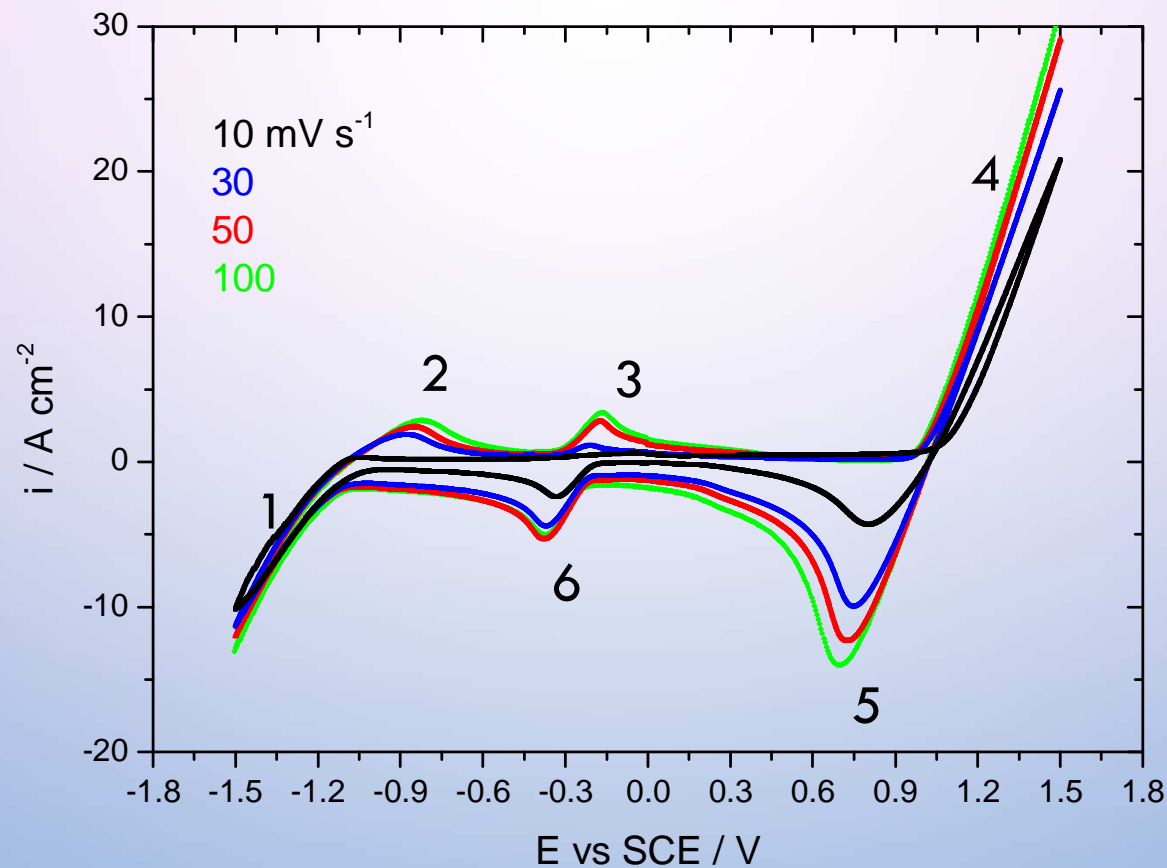


After 24 h in
ET + H₂O



CV Ethaline in Pt

(3 mm diameter Pt disk)



1. Water present?
 Water reduction.
 No water?
 Decomposition of DES?

2. Water present?
 H₂ oxidation after 1.
 No water?
 Reactions?

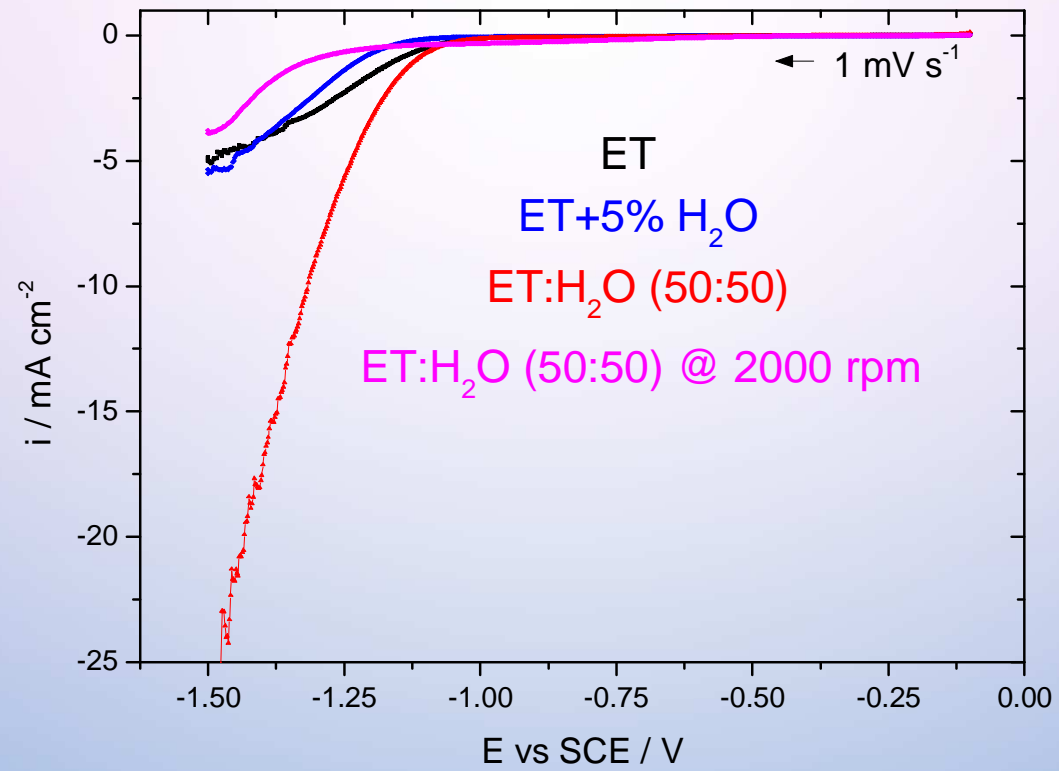
3. Chloride adsorption?
 Pt-O ?

4. Water present?
 Water oxidation.
 No water?
 Decomposition of DES.
 Cl⁻ → Cl₃⁻ (?)

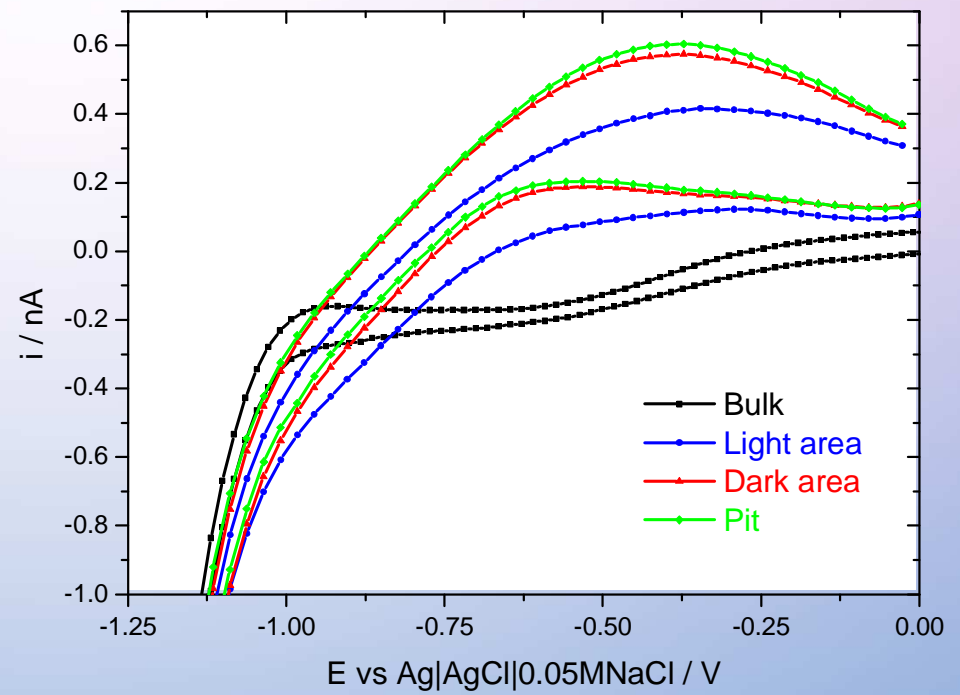
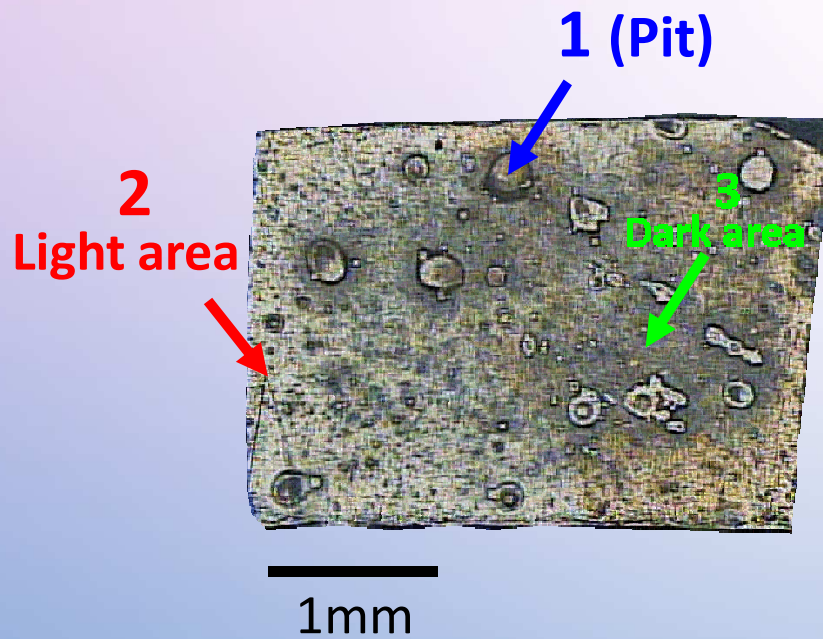
5. Reduction Pt-O?
 Reduction of products of 4?

6. O₂ reduction?

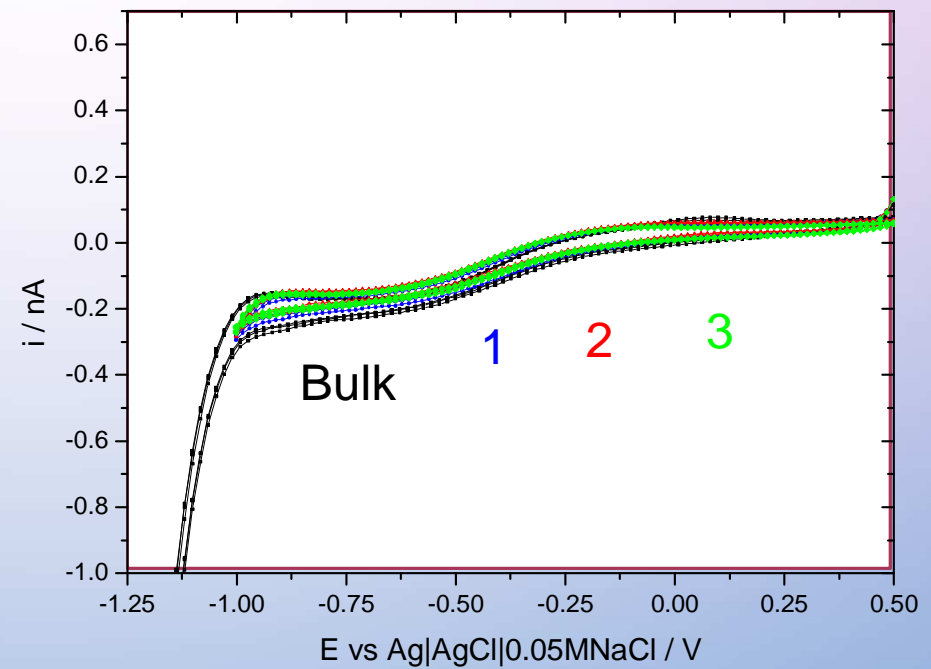
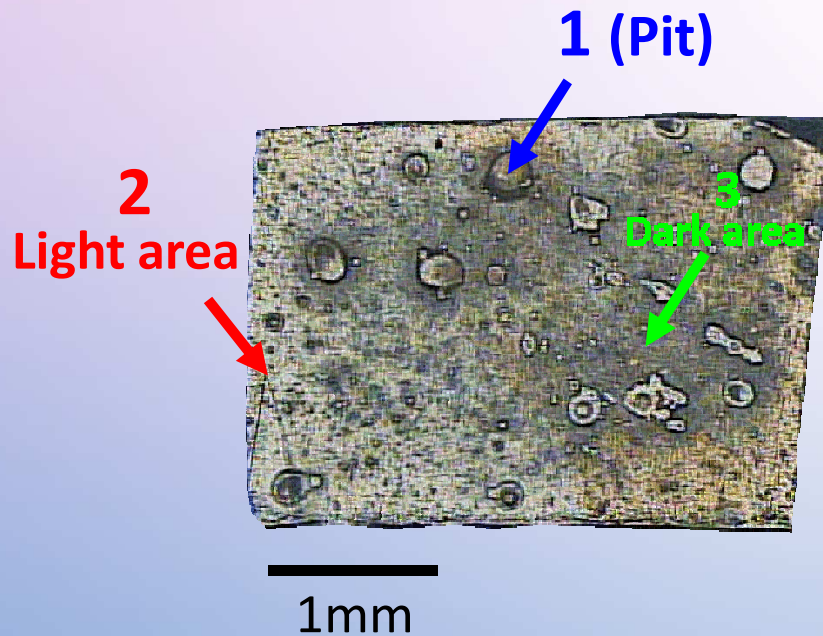
CV Ethaline in Pt



AZ31 6 days immersed in ethaline one to air

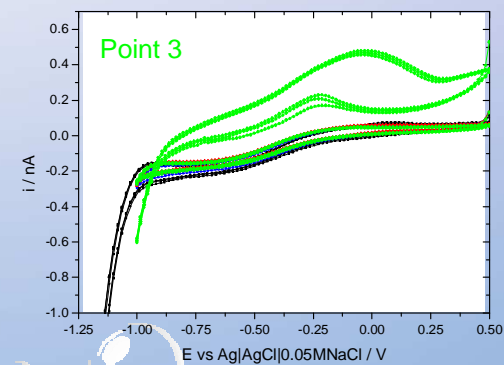
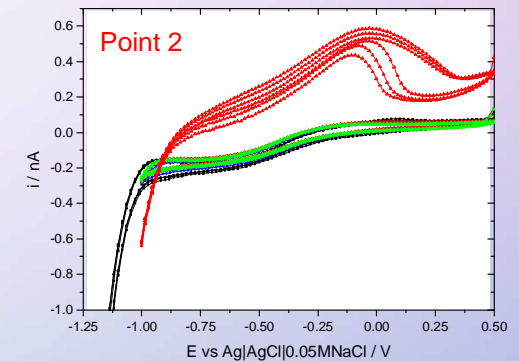
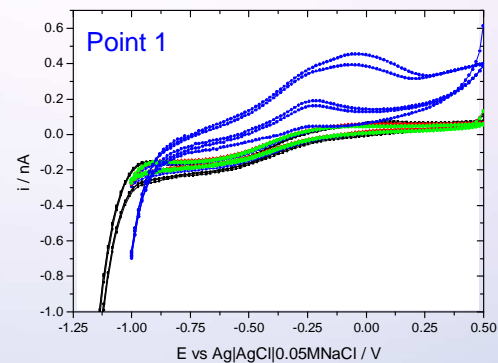
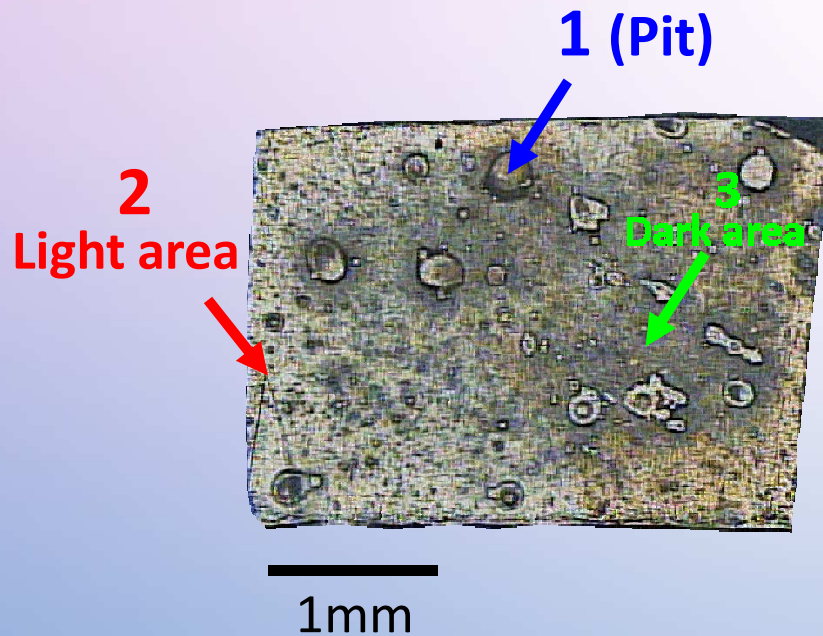


AZ31 6 days immersed in ethaline one to air
Replacing the solution by freshly prepared ethaline



AZ31 6 days immersed in ethaline one to air
Replacing the solution by freshly prepared ethaline

...and then, adding H₂O to 30% volume of the final solution...



CONCLUSIONS

- Very low corrosion of Mg and AZ31 in “pure” ethaline
- High tendency of ethaline to absorb water
- Corrosion of Mg and AZ31 takes place when ethaline contains water (> 5 mass %).

WHAT'S MISSING?

Electrochemistry of ethaline
(with and without water)

Karl-Fischer titration
(amount of water
inside ethaline)

**Surface and corrosion
products analysis**

SEM/EDS

XRD

XPS

FTIR/Raman

ACKNOWLEDGEMENTS

Mihael Bucko

COST Action n° MP1407

“The study of metal electrodeposition and metal corrosion
in deep eutectic solvents by SVET”

(25/03/2018 to 07/04/2018)

*Project **CICECO- Aveiro Institute of Materials***

POCI-01-0145-FEDER-007679

FCT Ref. UID/CTM/50011/2013)

FCT – Fundação para a Ciência e a Tecnologia (Portugal)

FEDER/ERDF - European Regional Development Fund

POCI/OCIP - Operational Competitiveness and Internationalization Programme

Other metals and alloys

Fe

Zn

Al

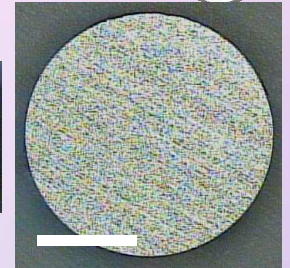
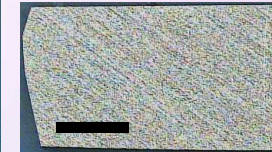
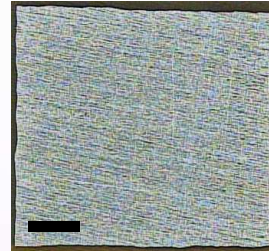
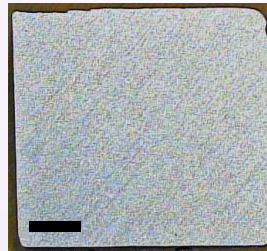
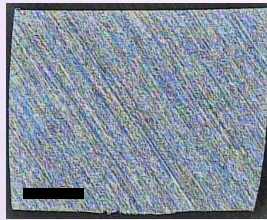
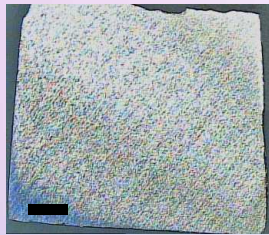
AA2024

Cu

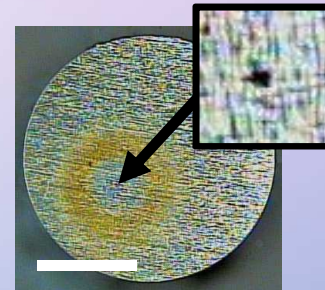
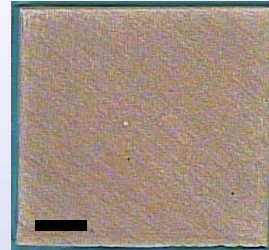
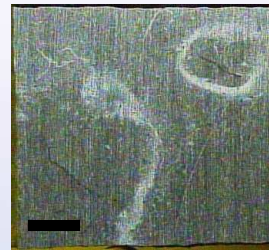
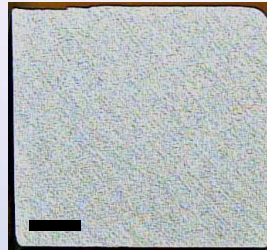
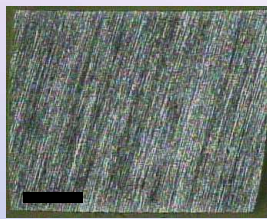
Brass
(Cu60Zn40)

SS304

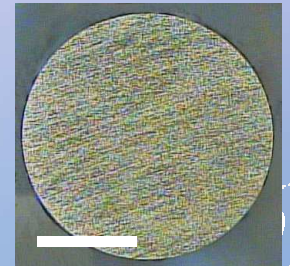
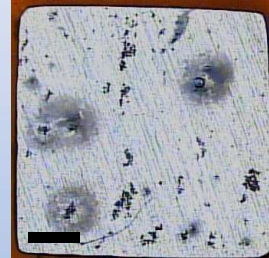
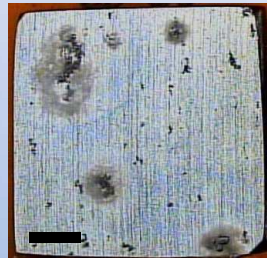
Before
test



20 days
in
ethaline
(closed)



20 days
in
ethaline
(open to air)



— Scale length = 1 mm